PATENT SPECIFICATION (11) 1373325

1373325

(21) Application No. 24695/73 (22) Filed 23 May 1973
(31) Convention Application No. 7 224 576 (32) Filed 30 June 1972 in (19)
(33) France (FR)
(44) Complete Specification published 13 Nov. 1974
(51) International Classification C07C 25/08
(52) Index at acceptance
C2C 220 227 22Y 313 31Y 338 43X 562 69Y 73Y HE

(54) SEPARATION OF THE META- AND PARA-ISOMERS OF DICHLOROBENZENE BY EXTRACTIVE DISTILLATION

(71) We, RHONE-PROGIL, a French body corporate of 6 Rue Piccini, 75016 Paris, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the separation of the 1,3- and 1,4- isomers of dichlorobenzene by extractive distillation.

It is known that the processes for the synthesis of dichlorobenzene by chlorination of benzene all lead to mixtures, in varying proportions, of the 3 isomers of dichlorobenzene. These mixtures also contain small amounts of compounds which contain more or less than 2 chlorine atoms per benzene ring, the elimination of which from the mixture of dichlorobenzenes poses hardly any problems because they have markedly different physical properties. In contrast, the isolation of each of the dichlorobenzene isomers is more delicate. However, the majority of the *ortho*-dichlorobenzene can generally be isolated quite easily by distillation because its boiling point is higher than those of the *meta*- and *para*- isomers, especially under reduced pressure. Thus what is left is a mixture of *meta*- and *para*-dichlorobenzenes which generally contain at most 30% of remaining *ortho*-isomer as well as a few parts per thousand of mono- and trichlorobenzenes.

Numerous difficulties have been encountered in the production of pure *meta*-dichlorobenzene from this mixture. In effect, simple distillation is not effective in practice because the boiling points of the *meta*- and *para*-isomers are very close. Furthermore, crystallisation methods only make it possible to obtain a *meta-para* eutectic containing 88 mol % of *meta*, whilst the molar concentration of *meta* in the *meta-para* mixture is less than 0.88. An alternative method of separation consists of brominating the dichlorobenzenes, separating the brominated isomers by distillation and then debrominating them (see, for example, United States Patent No. 3,170,961). It is clear that this method is complex and costly and only solves the problem very incompletely. The technique involving the use of molecular sieves (see, for example, United States Patent No. 2,958,708) is also hardly satisfactory because of the difficulties in regenerating such sieves and of their high cost.

The development, according to the present invention, of a simple method for the separation of *meta*- and *para*-dichlorobenzene, which makes is possible to obtain these compounds with a purity greater than 90%, thus provides the solution to a large technical problem as a result of the increase in the demand for pure *meta*-dichlorobenzene.

According to the present invention, there is provided a process for the separation of *meta*- and *para*-dichlorobenzene from a mixture containing them which comprises extracting *meta*-dichlorobenzene by extractive distillation in the presence of at least one aprotic polar solvent, and isolating *para*-dichlorobenzene from the aprotic polar solvent by distillation.

It will be appreciated that the selection of an extractive solvent is not easy. In effect, it is always very difficult to forecast which are the bodies which are capable of altering the relative volatility of the isomers sufficiently to make a separation by extractive distillation possible. Physical interactions and chemical effects between the solvent and the isomers are phenomena which are still very poorly understood at the present time, and those skilled in the art do not have any precise rule available to them which makes it possible for them to make a choice *a priori*. We have thus been surprised to find that aprotic polar solvents are particularly suitable for the separation of *meta*- and *para*-dichlorobenzenes by extractive distillation.

The mixture of the *meta*- and *para*-isomers of dichlorobenzene can consist of these two products alone. However, most frequently, it contains other chlorinated benzene compounds in a proportion which, however, does not

[Price 25p]

generally exceed 30% of the weight of the mixture. These other compounds are generally monochlorobenzene, *ortho*-dichlorobenzene and trichlorobenzenes synthesised during the manufacture of dichlorobenzene. Mono- and tri-chlorobenzenes are generally present only in small amounts, for example less than 0.5%.

The aprotic polar solvents are suitably those organic solvents which have a dielectric constant greater than 20 and a dipolar moment greater than 3.0 Debye. Although the use of a single solvent is generally simplest, it is possible to use a mixture of solvents to carry out the distillation.

Amongst the compounds which meet the necessary conditions, those which appear in the Table below are preferred. The values for the coefficient of relative volatility, measured during experiments carried out by means of a Hala ebulliometer under a pressure of 50 mm. of mercury, the molar ratio of solvent to dichlorobenzenes being 0.85, are given in this Table.

Aprotic polar solvent	Coefficient of relative volatility of *meta*- and *para*- dichlorobenzene
Hexamethylphosphorotriamide	1.20
Dimethylsulphoxide	1.175
N-Methylpyrrolidone	1.16
Dibutylsulphoxide	1.15

As described above, the process according to the invention comprises a stage in which the *meta*-dichlorobenzene is isolated followed by a stage in which the extractive solvent and *para*-dichlorobenzene are separated from one another.

The first stage is generally carried out as follows. The average relative proportions of dichlorobenzenes and aprotic polar solvent in the distillation column depend on the nature of the solvent and on the desired effectiveness. In general terms, the coefficient of relative volatility of the mixture of isomers increases with the proportion of solvent and the distillation capacity decreases when the proportion of solvent increases, all the other conditions remaining constant. The most appropriate molar ratio of solvent to dichlorobenzenes is thus a compromise. In general terms, it can be stated, however, that it will be between 0.2 and 5, and preferably approximately 1.

The extractive distillation can be carried out under atmospheric pressure, provided that the temperature necessary to cause the solvent to boil does not also bring about its degradation. Since the aprotic polar solvents which are currently used industrially are relatively sensitive to temperature, the distillation is preferably carried out under reduced pressure. Moreover, the coefficient of relative volatility of the *meta-para* mixture decreases when the pressure increases, and this decreases the effectiveness of the distillation. For both these reasons, the pressure at the foot of the column is desirably below 120 mm. of mercury.

The choice of column to be used is guided by two factors. Firstly, it must be possible for the column to operate under low pressure; secondly, the column must possess a large number of theoretical plates because of the low value of the coefficient of relative volatility. A low pressure and a large number of theoretical plates lead to a choice of columns, the packing of which gives a low pressure drop. Amongst the columns which possess these properties, columns with a knitted packing and columns in which the packing is a metal gauze with a geometric structure are known. All the other characteristics of the column, such as its dimensions and the degree of refluxing can be determined easily by those skilled in the art.

The second stage of the process, which consists of separating the extractive solvent from the *para*-dichlorobenzene and, where appropriate, from *ortho*-dichlorobenzene which may be present, is a conventional distillation operation which can be carried out easily because of the considerable difference in physical properties of each of the products present.

The following Example further illustrates the present invention. The Figure in the accompanying drawing illustrates a typical embodiment, in diagrammatic form, of apparatus suitable for carrying out the process.

EXAMPLE.

A distillation column 1, of height 20 m. and diameter 600 mm., is packed with a metal gauze of geometric structure the characteristics of which are as follows:

Specific surface area:	0.5 m^2/litre
Height equivalent to 1 theoretical plate:	200 mm.
Pressure drop per theoretical plate:	0.4 mm. Hg

This column is supplied at the rate of 70 kg./hour *via* a pipeline 2 with a mixture of equal amounts, by weight, of *meta*- and *para*-dichlorobenzenes and at the rate of 1,000 kg./hour *via* a pipeline 3 with H.M.P.T. (Hexamethylphosphorotriamide) which is drawn off at the foot of a column 7 and pumped into tank 4 and heated in exchanger 10. When the pressure at the head is established at 40 mm. of mercury, the temperature at this point is 83°C, whilst at the foot the pressure is 75 mm. Hg and the temperature is 150°C. *Meta*-dichlorobenzene is drawn off *via* pipeline 5 (purity 99%) and recycled with a degree of refluxing of 18. Under these conditions, the average molar ratio of solvent to dichlorobenzenes in the liquid phase of the column is approximately 1.5. The mixture of *para*-dichlorobenzene and H.M.P.T., drawn off at the foot 6, of the column, is injected into column 7 (height 4 metres, diameter 300 mm., same packing as 1). When the pressure at the head of this column is steady at 40 mm. Hg and the temperature is 84°C, whilst at the foot the pressure is 47 mm. Hg and the temperature is 151°C., *para*-dichlorobenzene is drawn off *via* pipeline 8 (purity 95%) and recycled with a degree of refluxing of 4. The H.M.P.T. drawn off at the foot of column 7 is conveyed back to the column 1.

WHAT WE CLAIM IS:

1. Process for the separation of *meta*- and *para*-dichlorobenzene from a mixture containing them which comprises extracting *meta*-dichlorobenzene by distillation in the presence of at least one aprotic polar solvent, and then isolating *para*-dichlorobenzene from the aprotic polar solvent by distillation.

2. Process according to claim 1 in which the extractive distillation of the *meta*-dichlorobenzene is carried out under a pressure of less than 120 mm. of mercury.

3. Process according to claim 1 or 2 in which the extractive distillation of the *meta*-dichlorobenzene is carried out in a distillation column having a knitted or metal gauze packing.

4. Process according to any one of the preceding claims in which the aprotic polar solvent has a dielectric constant greater than 20 and a dipolar moment greater than 3.0 Debye.

5. Process according to any one of the preceding claims in which the aprotic polar solvent is hexamethylphosphorotriamide, dimethylsulphoxide, dibutylsulphoxide or N-methylpyrrolidone.

6. A process according to any one of the preceding claims in which the ratio of solvent to the mixture is between 0.2 and 5.

7. Process according to any one of the preceding claims in which the mixture also contains *ortho*-dichlorobenzene.

8. Process according to claim 1 substantially as hereinbefore described with reference to the Figure of the accompanying drawing.

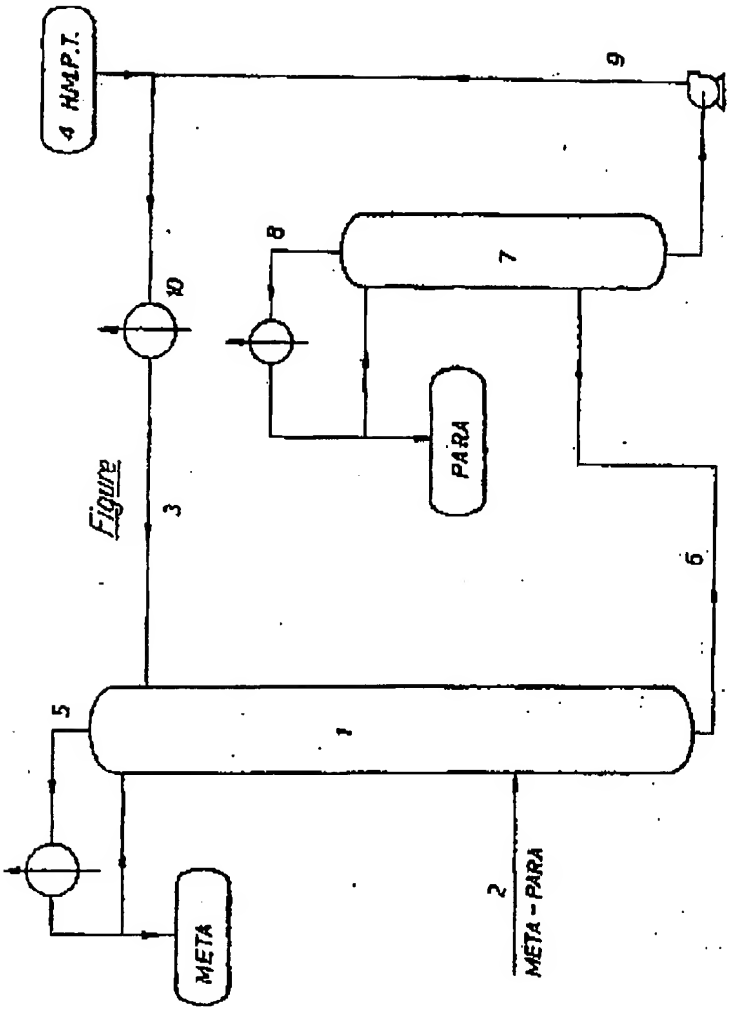
9. *Meta*-dichlorobenzene whenever isolated by a process as claimed in any one of claims 1 to 8.

10. *Para*-dichlorobenzene whenever isolated by a process as claimed in any one of claims 1 to 8.

J. A. KEMP & CO.,
Chartered Patent Agents,
14, South Square,
Gray's Inn, London, W.C.1.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1974.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1373325 COMPLETE SPECIFICATION
1 SHEET This drawing is a reproduction of the Original on a reduced scale



Figure